MODE OF OCCURRENCE OF TRACE ELEMENTS IN COAL

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE

REQUIREMENTS FOR THE DEGREE OF

Bachelor of Technology

In

Mining Engineering

By

SABYASACHI PRAKASH

Roll: 108MN006

DEPARTMENT OF MINING ENGINEERING

NATIONAL INSTITUTE OF TECHNOLOGY

ROURKELA - 769008

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CERTIFICATE

This is to certify that the thesis entitled "**MODE OF OCCURRENCE OF TRACE ELEMENTS IN COAL**" submitted by Sri Sabyasachi Prakash, (Roll No. 108MN006) in partial fulfilment of the requirements for the award of Bachelor of Technology degree in Mining Engineering at the National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/Institute for the award of any Degree or Diploma.

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ACKNOWLEDGEMENT

I wish to express my profound gratitude and indebtness to Asst. Prof. Sk. Md. Equeenuddin, Department of Mining Engineering, NIT, Rourkela for introducing the present topic and for their inspiring guidance, constructive criticism and valuable suggestions throughout the project work.

I am also thankful to Prof. Upendra Kumar Mohanty, Department of Metallurgical and Material Science, Prof. Dilip Kumar Pradhan, Department of Physics and Prof. (Mrs.) Kakoli Karar (Paul)**,** Department of Civil Engineering for their assistance and help in carrying out different experiments in various laboratories.

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ABSTRACT:

More than half of the country's energy needs are fulfilled by coal. Besides power generation coal is also used in many other industries for production of cement, steel, etc. With the increasing usage of coal, the harmful impact of coal on environment cannot be neglected. Besides producing green house gases and other toxic fumes, the high metal content in coal pose a major threat to environment as well as life.

Trace elements are present in very low percentage in coal but their concentration increases manifold after coal combustion and utilization. Throughout the process of coal production as well as consumption, trace elements are released from coal. Their release into the surrounding atmosphere largely depends on the nature of their association with coal, also known as, their modes of occurrence. Basically, trace elements are present in the mineral matter but studies also show that some may be directly present in the organic matrix. Their hazardous impact on environment emphasises more detailed study in this field. In this project efforts were made to study some trace elements namely - Ni, Mn, Cr, Cu, Zn and Pb in coal samples from Mand-Raigarh coalfield, Chhattisgarh; Rangit valley, Sikkim; and Neyveli lignite, Tamil Nadu. Quartz and clay minerals were predominant in all the coal samples. Nickel and Cr are present in higher concentrations in all coal samples. Copper, Pb and Zn were associated with sulphides and disulphides. Chromium and Ni are organically associated in Neyveli lignite. Primary mode of occurrence of Mn is concluded to be as carbonates.

Chapter-1

INTRODUCTION

1.1 INTRODUCTION:

Coal has been used as a source of energy by many ancient civilisations. Scholars date back the use of coal to ancient China as early as 1000 B. C. During the industrial revolution, coal was considered to be an important source of energy for industries. Since then, coal has become the major source of energy of the world (Miller, 2011).

India has fourth largest coal reserves in the world of around 287 billion tonnes. The United States, Russia and China are the three countries with higher coal reserves than India. India is the third largest producer of coal in the world with around 532 million tonnes of coal production in the year 2009-10. About 70% of the coal produced is utilized for power generation in the country. About 68% of the country's energy needs are fulfilled by coal. Besides power generation, coal is also used in many other industries such as cement, steel, fertilizer, chemical and paper. Coal is also a domestic fuel used in households for cooking and heating purposes (National Statistical Organisation, 2011).

Elements with concentrations of 100 ppm or less in coal are considered to be trace elements (Raask, 1985). Trace elements are present in coal within the organic matrix or as mineral matter. They are introduced into the coalification process by the interaction of the decaying plant matter with solutions entering the swamp in a reducing environment, settling of minerals in the solution as well as decomposition and mutual reaction between minerals, along with the concentrating effects of some plants and the inherent characteristic of elements to chemically bind themselves with the organic matter (Swaine and Goodarzi, 1995).

Trace elements of concern include, among others, Pb, Cr, As, Hg, Sb, Cd, Co, Cu, Ni and Se. Many of the trace elements are radio-active such as U, Th, etc. and pose radioactive hazards. Mode of occurrence of elements in coal relates to their association with various solid components. Furthermore, mode of occurrence of an element plays a major role in predicting its behaviour during the processes of coal production, its utilisation and waste disposal. Trace elements that are weakly bound (in the form of adsorbed or exchangeable) may be readily leached into water or mildly acidic solution, hence, causing damage to the surrounding eco-system. Whereas, those strongly bonded with coal (associated with clay minerals, silicates or organic matrix) may be concentrated in the ash, hence, requiring further treatment before its disposal. Mode of occurrence may vary from element to element and also, some element may have multiple modes of occurrences. The concentration of trace elements and their

modes of occurrences vary from coal to coal. This further emphasises the importance of determining their concentrations in all major coalfields.

Many of these elements are environmentally sensitive. When introduced into the human body in concentrations greater than the permissible limit, they cause a wide range of diseases and health hazards ranging from nausea, stomach aches to cancers and brain damage. Due to the rising concern over their ill-effects on environment and human health, trace elements have attracted much attention in the past few years.

1.2 OBJECTIVE:

The objective of this project is to determine

1. Mineralogy of coal
2. Concentration of Ni, Mn, Cr, Cu, Pb and Zn in coal
3. Modes of occurrences of Ni, Mn, Cr, Cu, Pb and Zn in coal

Chapter-2

LITERATURE REVIEW

2.1 MINERALOGY OF COAL:

Coal is a sedimentary rock. It is mainly composed of following categories of substances in various proportions:

- Organic carbonaceous matter (termed macerals)
- Inorganic (mainly crystalline) minerals
- Fluids

The fluids in coal prior to mining are mainly moisture and methane. In terms of coal analysis, the term mineral matter is an inclusive term that refers to the mineralogical phases as well as to all other inorganic elements in the coal; that is, the elements that are bonded in various ways to the organic components. The term mineral refers only to the discrete mineral phases. As coal is a type of sedimentary rock, 100 or so different minerals can occur in coal; however, only some are abundant enough to have high importance. These are listed in Table 2.1 along with the stoichiometric chemical formula of each. Minor impurities commonly substitute for the cations as well as some anions which account for a considerable fraction of the minor and trace elements reported in coals (Harvey, 1984).

In the average coal, clay minerals may constitute up to 60 weight percent of the mineral matters, with up to 20 weight percent being common. The carbonate minerals (calcite, siderite and to a lesser extent, dolomite and ankerite) and the iron disulphide minerals (pyrite and marcasite) make up, on the average, about 10 weight percent in each group. Sulphate minerals of calcium and iron, and the feldspar minerals are commonly present but rarely in concentrations of more than a few weight percent. Except for unusual cases such as the sulphide rich coals of the marine origin, the occurrence of the other minerals in concentrations exceeding a few percent is rare (Renton, 1977).

The minerals listed in Table 2.1 are classified by their physical modes of occurrences. Description of mineral impurities in coal deposits, based on this classification is useful in a number of ways. Thick layers and abundant nodules of rock fragments hamper mining operations, but are removed by standard coal cleaning facilities. On the other hand, disseminated minerals and the thinner (microscopic) layers cannot be removed by existing preparation facilities. The latter two modes are dominated by mixtures of illite, quartz, and pyrite. According to genesis (Mackowsky, 1982) minerals in coal can be classified as detrital,

syngenetic, or epigenetic (Table 2.1). Detrital minerals are those that were deposited in a coal forming peat swamp from slowly moving water or wind currents (Harvey, 1984).

Table 2.1 Minerals present in coal (Harvey, 1984).

Mineral group	Minerals	Composition	Chief occurrence		Abundance in mineral matter
			Physical*	Genetic**	
Clay minerals	Illite (sericite,K-mica)	$KAl_2(AlSi_3O_{10})(OH)_2$	D,L	d,s	common
	Smectite (mixed layered)	$Al_2Si_4O_{10}(OH)_2.H_2O$	D,L	d,s	common
	kaolinite group	$AL_2Si_4O_{10}(OH)_8$	L,F	e,d,s	common
Sulphides	Pyrite	FeS_2 (isometric)	D,N,F	s,e	variable
	Marcasite	FeS_2 (orthorhombic)	D	s	rare
	Sphalerite	ZnS	f	e	rare
Carbonate	Calcite, Dolomite, Ankerite (Fe)	$CaCO_3$ $Ca(Mg, Fe)(CO_3)_2$	N,F N	e,s s,e	variable variable
	Siderite	$FeCO_3$	N	s,e	variable
Oxides	Haematite	Fe_2O_3	N	s	rare
	Quartz	SiO_2	D,L,N	d	common
Others	Limonite-Goethite	FeO(OH)	N	e	rare
	Apatite	$Ca_3(PO_4)_3(F,Cl,OH)$	D	d,s	rare
	Feldspars	$K(Na)AlSi_3O_8$	D,L	d	rare
	Zircon	$ZrSiO_4$	D,L	d	rare

Legend:

- *D = disseminated; L = layers (partings); N = nodules; F = fissures (cleat).
- **d = detrital;
- e = epigenetic; second state of coalification (mainly along joints (cleat) in coal beds);
- s = syngenetic, first stage of coalification (disseminated intimately intergrown with macerals)

Flakes of illite clay and microscopic grains of quartz, feldspars, zircon, apatite, rutile and perhaps others were deposited as discrete grains which became interbedded with peat and ultimately with the resultant coal. Most wind deposited minerals are recognised as such by the presence of certain high temperature phases. These are therefore, dust particles derived from distant volcanoes. Layered deposits of these dusts are termed tonsteins. Syngenetic minerals are those that formed within the peat during the early stages of its coalification – before the peat was deeply buried by other sediments, probably by not more than about 50 feet. Under these conditions disseminated pyrite is thought to have formed in sulphate bearing peat by bacterial reduction of sulphur. Much of this type of pyrite has a spherical form and is described as framboidal pyrite. Nodules of peat mineralized with various carbonates and nodules comprised of microcrystalline quartz and/or haematite formed early in the development may also be syngenetic in origin, notably micrometer sized crystals of kaolinite and possibly illite. These crystallites, as well as some of the tiny disseminated grains of quartz are thought to have crystallized from inorganic matter inherited from the original plant material. Epigenetic minerals are mainly those found in fissures and void fillings. Much of the calcite in coal as well as part of the pyrite and kaolinite in coal is recognized as epigenetic. This class of minerals formed long after peat was consolidated and coalified enough to allow joints to develop wherein these minerals precipitated. For most coals, precipitation probably occurred during the late lignite or early sub-bituminous stages of coalification (Harvey, 1984).

2.2 MODE OF OCCURRENCE OF TRACE ELEMENTS:

Mode of occurrence of a trace element is a description of the manner in which an element is chemically attached to the host rock/material (Finkelman and Gross, 1998). Trace elements may be organically or inorganically associated with coal. Inorganic association is mainly due to the mineral matter present in coal which may vary in proportion from coal to coal. Finkelman (1982) suggested that organic association will predominate in coals with low ash yields, i.e. less than about 5%. Trace elements may be attached to certain organic functional groups namely, carboxylic acid (-COOH), phenolic hydroxyls (-OH), mercapto (-SH), imino (=NH) etc. For most coals, trace elements occur with mineral matter, as discrete minerals, either as free or embedded in organic matter, as replacement ions in minerals and adsorbed on the minerals (Swaine and Goodarzi, 1995).

Table 2.2: Likely mode of occurrence of 6 trace elements found in coal and of level of confidence estimate (Swaine and Goodarzi, 1995).

Element	Mode of occurrence	Level of confidence
Cr	Organic or clay association	2
Cu	In chalcopyrites	8
Pb	In galena	8
Ni	Multiple associations	2
Zn	Sphalerite	8
Mn	In carbonates, siderite and ankerite	8

Likely modes of occurrence of the elements under this study with corresponding level of confidence are given in Table 2.2. The estimation of the level of confidence in the assessment of its mode of occurrence has been done by numerical scaling from 1 to 10; 1 indicating no or least confidence while 10 indicating the highest level of confidence. This estimate is largely based on whether the mode of occurrence was determined by direct (Scanning Electron Microscope (SEM), Atomic Absorption Spectrophotometer (AAS), etc) or indirect methods (float-sink data). Another factor contributing to the confidence level is how consistently the particular element has behaved in various studies (Swaine and Goodarzi, 1995).

Table 2.3: Trace metal concentration in Gondwana coals of India (Narsimhan and Mukherjee, 1999) (Unit: mg/kg)

Element	Damodar Koel Valley		Sone-Mahanadi Valley		Pench Kanhan Valley		Wardha Godavari Valley	
	Range	Avg.	Range	Avg.	Range	Avg.	Range	Avg.
Ni	0-100	28	3.2-56	25.4	11.4-34.6	22.7	12.9-40.4	25
Cr	10-136	47.5	12.2-97.1	43.2	26.9-42.4	33.7	24.9-90.5	54.5
Cu	4.2-54	21.4	15.5-65	32.1	18.9-31	24.3	13-67.1	29.5
Zn	8.1-81	33.3	6.4-108	30.8	8.4-54.2	26.0	7.3-75.4	29.2
Pb	0-40.2	17.9	0-46.5	15.4	8.4-12	10.2	0-13.7	1.5
Mn	33-150	57.6	24.9-228	90.5	54.5-150	85.0	10.5-153.7	58.6

Table 2.3 and 2.4 show the trace element concentrations for different coals of India and outside. The range of coal samples considered for characterisation for Table 2.3 covers mainly 4 coal basins namely- Damodar-Koel valley, Sone-Mahanadi valley, Pench-Kanhan valley and Wardha-Godavari valley of the Gondwana coals of India. In Table 2.4, a

comparison is made between Gondwana coals, coals of Australia, the US and world average (Narsimhan and Mukherjee, 1999).

Table 2.4: Average trace element concentration in different coals (Narsimhan and Mukherjee, 1999) (Unit: mg/kg)

Element	Indian average	US average	Australian average	Worldwide average
Ni	45	15	15	15
Cr	70	15	6.0	10
Zn	40	39	25	50
Pb	15	16	10	25
Cu	20	19	1.5	15
Mn	100	100	----	50

The mode of occurrence of an element can have a strong impact on its behaviour during coal cleaning, weathering, leaching, combustion and conversion. The different modes of occurrences will cause the element to detach itself from the host material into the surroundings, in specific favourable surrounding environment and thus, will have different environmental and health impacts. The use of coal having trace elements with low concentration could still result in detrimental environmental impact if mode of occurrence allows the element to be readily released during utilisation (Finkelman and Gross, 1998).

Some trace elements may be beneficial for the environment while others may have hazardous effects. For example- calcium, potassium, magnesium etc are present in coal in minor or trace quantities but they are a source of nutrients to plants. Elements such as arsenic, selenium, Pb, Cr, Ni, cadmium, mercury etc. can have toxic effects on the surrounding environment as well as life. Cadmium and mercury are both toxic and carcinogenic in nature. Intake of abnormal concentrations of Pb could lead to damage to the central nervous system. Selenium is toxic to plants. Arsenic is toxic even in small concentrations. It can cause anaemia, gastric disturbances, renal symptoms, and skin and lung cancers. In addition, it also damages peripheral nerves and blood vessels and adversely affects embryos and foetuses. Beryllium is toxic and carcinogenic. It also causes lymphatic, liver, spleen and kidney problems and respiratory diseases. Excess intake of fluorine may cause fluorosis and osteoschlerosis (Miller, 2011).

The oxidation state of Cr affects its mobility in the environment. Cr III is non-toxic and is readily absorbed into clays, sediments and organic matter and thus is not very mobile. Cr IV

is more mobile and toxic and thus is more dangerous even in small concentrations (Miller, 2011).

Dreher and Finkelman (1992) found seven different forms of selenium in coal and overburden while studying the cause of high levels of selenium in the back-fill ground water in Powder River Basin coal mine. Selenium was both organically and inorganically associated. Organically bound selenium was found to be around 75% of total selenium. However, Dreher and Finkelman (1992) concluded that oxidation of pyrite was the major cause of high levels of selenium in the water although pyrite contained only 10% of the selenium (Finkelman and Gross, 1998).

Arsenic poisoning occurred in Guizhou province of China due to domestic combustion of As-bearing coal. During combustion of the coal, arsenic is volatilised and adsorbed on the food being cooked over the unvented coal fires (Zheng et al., 1996). Chilli peppers that were being dried seemed to be especially prone to arsenic adsorption. Fresh chilli peppers contain less than 1 ppm arsenic, whereas those dried over the coal fires contain an average of 500 ppm. Belkin et al. (1997) found seven different forms of arsenic in those coals. The chilli peppers was a staple in their diet and appeared to be the primary mode of arsenic poisoning.

2.3 STUDY AREA:

2.3.1 RANGIT VALLEY, SIKKIM:

Rangit valley coal spans across the state of Sikkim and some parts of West Bengal. With total area coverage of nearly 120 sq. km., the coal reserves have been assessed to be about 101.23 million tonnes. The rank of coal found here is semi-anthracite which is of Permian age. (ibm.nic.in/coalandlignite.pdf). The proximate analysis of coal samples from Rangit valley indicate following variation in moisture 3.14-6.31%, volatile matter 6.40-11.84%, ash 15.34-24.92% and fixed carbon 59.78-70.30% (Ghosh, 1952).

The coal-measure of Rangit valley constitutes light and dark grey, felspathic and gritty sandstones, carbonaceous slates and semi-anthracitic coal. At their base, tillite and varved slates are present. These are embedded with boulders and pebbles of gneiss, granite, quartzite, phyllite, chert and limestone. This type of formation can be compared to the glacial Talchir boulder bed present at the base of the lower Gondwana beds of the Indian peninsula.

A number of coal seams have been found in this area. There thickness ranges from a four feet to nearly 25 feet. These seams exist on hill tops as well as in the beds of the Rangit River and its tributaries. Due to the compressive and shear forces present, coal is hard and stony at places while being flaky, powdery and soft at other places respectively. The coal measures are intercepted by sills and dykes of mica-lamprophyre. The sequence of strata around the coal fields is inverted. The dip of the seams varies from 15º to 80º. Dip direction ranges from east to north-east on the eastern side and to west to north-west on the western side of the river. Due to the folding of a gigantic recumbent anticlinal structure, there is a wide variation in dip and strike direction as well as inverted stratigraphy (Ghosh, 1952).

2.3.2 MAND – RAIGARH COALFIELDS, CHHATTISGARH:

With an area of over 3700 sq. km., the Mand – Raigarh coalfields form almost all of the central part of the Son – Mahanadi basin. It lies between Hasdeo – Arand Coalfields in the north – west separated by a basement high and IB river coalfield in the south – east. Located in the Raigarh district of Chhattisgarh, the Mand – Raigarh coalfields extends from latitude 21º45' N to 22º42' N and longitude 83º01' E to 83º44' E (EIMP report, M/s DB Power Ltd. 2010). The coal reserves have been assessed to be about 21.55 billion tonnes. The rank of the coal found in this coalfield is sub – bituminous which is of Permian age (Holloway et al., 2007).

Stratigraphically, the area comprises of mainly two distinct broad litho units. They are the lower Gondwana group of rocks and the Precambrian Metamorphics separated by an unconformity. The Archaean Basement is the bottom – most layer. The Talchir Formation lies over the Archaean basement separated by an unconformity. The Karharbari measures lie over the Talchir Formation. Karhabari measures is overlain by Barakar measures which in turn is overlain by the Kamthis, which is the top – most formation of the Lower Gondwana group of rocks (Rao, 1982). The main coal bearing horizon is the Barakar measures of the lower Gondwana group. The proximate analysis of the samples from this coalfields indicate a variation in moisture from 4.0 % to 6.0 %, volatile matter from 21.0 % to 39.0 %, ash from 5.0 % to 33.0 % and fixed carbon from 33.0 % to 59.0 % (Singh et al., 2010).

2.3.3 NEYVELI LIGNITE FIELD, TAMIL NADU:

With an expanse of over 480 sq. km. and lignite reserves of 3.3 billion tonnes, the Neyveli lignite reserve is the largest lignite reserve in India. It extends from latitude 11º15' N to 11º40' N and longitude 79º25' E to 79º40' E. It is situated in the Ariyalur – Pondicherry sub – basin or South Arcot basin of the main Cauvery basin on the east coast at Neyveli. The lignite field is arch shaped with its apex towards the north – east direction (Singh et al., 1992).

Neyveli Formation is overlain by Cuddalore formation. The sub-surface litho stratigraphic unit can be divided into two parts, namely, Neyveli formation and Cuddalore formation (Siddhanta, 1986). Neyveli formation is overlain by the Cuddalore Formation. Neyveli Formation is of Miocene epoch of the Tertiary period. It comprises of semi – consolidated sandstone and clay beds. There are occasional limestone intercalations followed by 1 m thick carbonaceous clay and brown lignite. Lignite present in Neyveli formation may be up to 20 m thick. The Cuddalore formation constitutes ferruginous arcosic semi – consolidated sandstone with varying thickness of 60 – 120 m (Agarwal et al., 2008). The proximate analysis of samples from Neyveli Formation shows the moisture to be 53.0%, ash to be 3.0 %, volatile matter to be 24.0% and fixed carbon to be 20.0 %. The ultimate analysis shows the carbon percentage to be 69.30%, hydrogen percentage to be 5.65%, nitrogen percentage to be 0.40%, sulphur percentage to be 1.20% and oxygen percentage to be 23.45% (Singh et al., 1992).

Chapter-3:

METHODOLOGY

3.1 SAMPLE COLLECTION:

Coal samples were collected from Rangit Valley, Sikkim; Neyveli Lignite, Tamil Nadu, and Mand – Raigarh Coalfields, Chhattisgarh. Samples were crushed and sieved through a 230 mesh (< 63 μm) sieve. Powdered samples were kept in sealed packets for further analysis.

3.2 MINERALOGY STUDY:

Low Temperature Ashing (LTA) of Lignite sample was carried out because of the presence of very less ash content. Lignite sample was taken in a porcelain crucible and heated in a muffle furnace at 180°C for 48 hours. Whole coal samples were used for other two locations. All the three samples were then analysed in X – Ray Diffractometer (PANalytical X'Pert) for determination of the mineralogy. This analysis was carried out with a step size of 4 and speed of rotation of 1.2°/min. Intensity versus 2θ (in degrees) graphs was obtained. Then minerals were identified with the help of JCPDS file.

3.3 TRACE ELEMENT ANALYSIS:

Two gms of coal samples were measured and put in the respective volumetric flasks, which was thoroughly cleaned with dilute HNO_3. Coal samples were digested using mixture of concentrated HNO_3, HF and H_2O_2 on hot plate inside the fume hood. After digestion samples were cooled, diluted and filtered using a 0.22 μ (micron) filter paper. Filtrate was then analysed using Atomic Absorption Spectrophotometer (AAS, Perkin Elmer).

3.4 DETERMINATION OF MODE OF OCCURRENCE:

A flask was properly rinsed first with mild acid and then with distilled water. Mode of occurrence was studied using the fractionation study following the method of Finkelman, (1990). 4 gms of coal sample of each coal sample was subjected to sequential leaching first with 25 ml of 1 N ammonium acetate (NH_4OAc) followed by 25 ml of 3 N Hydrochloric acid (HCl), 25 ml of 2 N HNO_3 and 25 ml of 48% HF. Each sample was agitated at room temperature in each of the solvents for 18 hours. Each solution was then filtered using a 0.22 μ (micron) filter paper into a bottle and labelled. The filtrates were then analysed in AAS to determine the concentration of each element in each filtrate.

Chapter-4:

RESULTS AND DISCUSSIONS

4.1 MINERALOGY:

Results of the XRD analysis of coal samples of Rangit valley, Neyveli lignite and Mand-Raigarh coalfields are shown in Figures 4.1, 4.2 and 4.3 respectively.

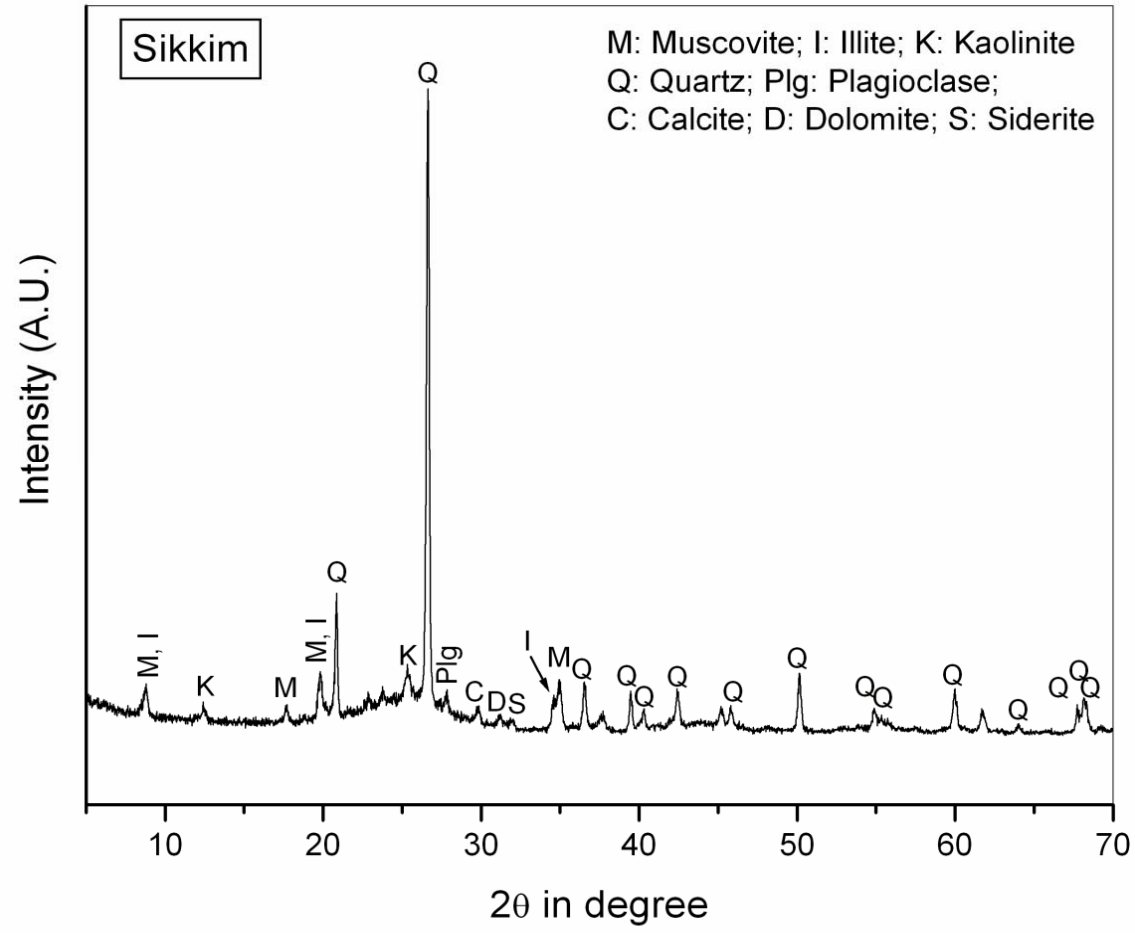

Fig.4.1 XRD pattern of Rangit Valley, Sikkim

Quartz [SiO_2] was the pre-dominant mineral phase present in the sample from Rangit valley, Sikkim (Fig. 4.1). Other major mineral phases include muscovite [$KAl_2(AlSi_3O_{10})$ $(F,OH)_2$] and illite [$(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}((OH)_2,(H_2O))$]. Kaolinite [$Al_2Si_2O_5(OH)_4$], plagioclase [$NaAlSi_3O_8$], calcite [$CaCO_3$], dolomite [$CaMg(CO_3)_2$] and siderite [$FeCO_3$] were also present in the sample as intermediate mineral phases.

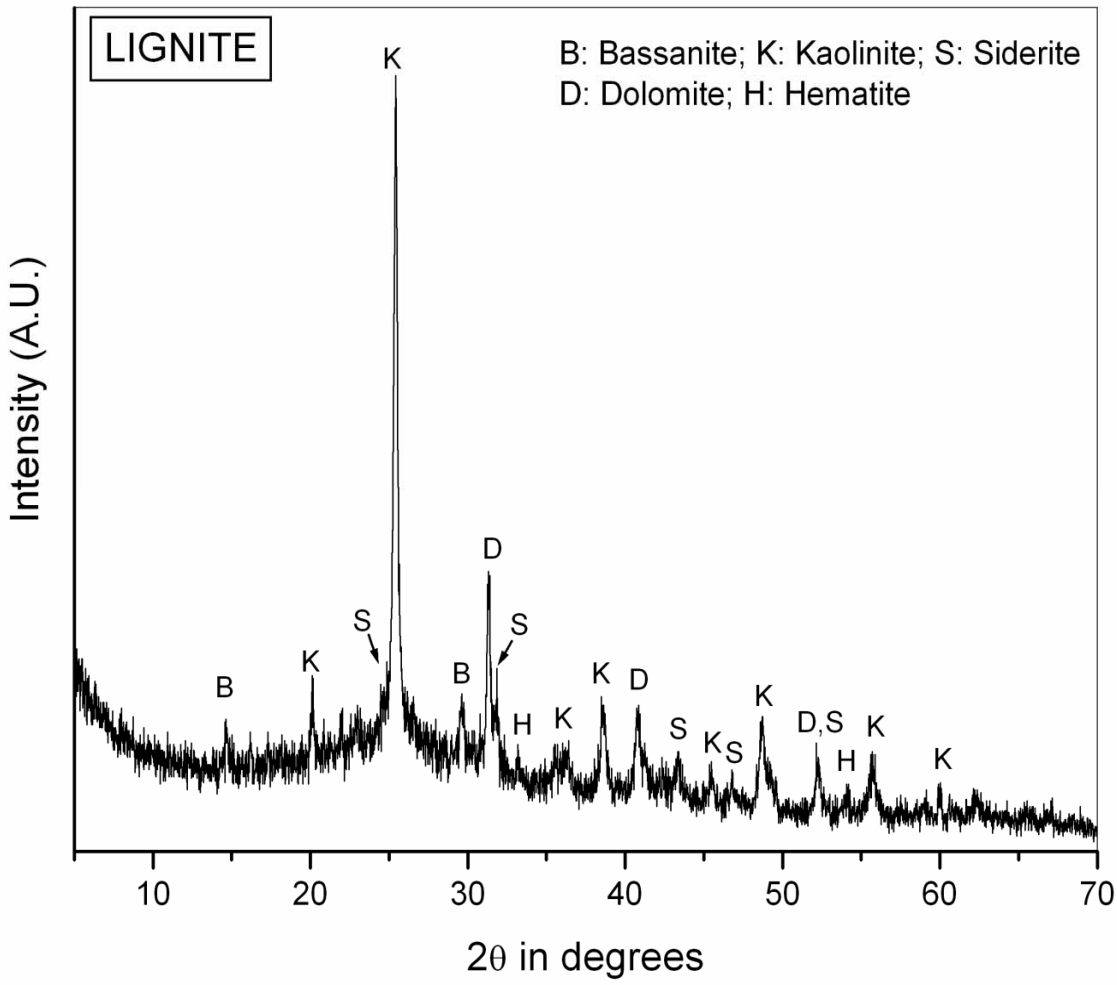

Fig. 4.2 XRD pattern of Neyveli lignite field

The XRD analysis of the coal sample from Neyveli lignite field indicates the dominance of clay minerals and carbonate phases (Figure 4.2). The major mineral phases found in this coal are kaolinite, dolomite and siderite. Bassanite [$2CaSO_4.H_2O$] and haematite [Fe_2O_3] were found to be present in intermediate phases.

X-ray diffractogram of Mand-Raigarh coal is given in Figure 4.3. The major mineral phases in Mand – Raigarh coalfield include quartz and kaolinite. Goethite [FeO(OH)], siderite and plagioclase were found to be present in intermediate mineral phases.

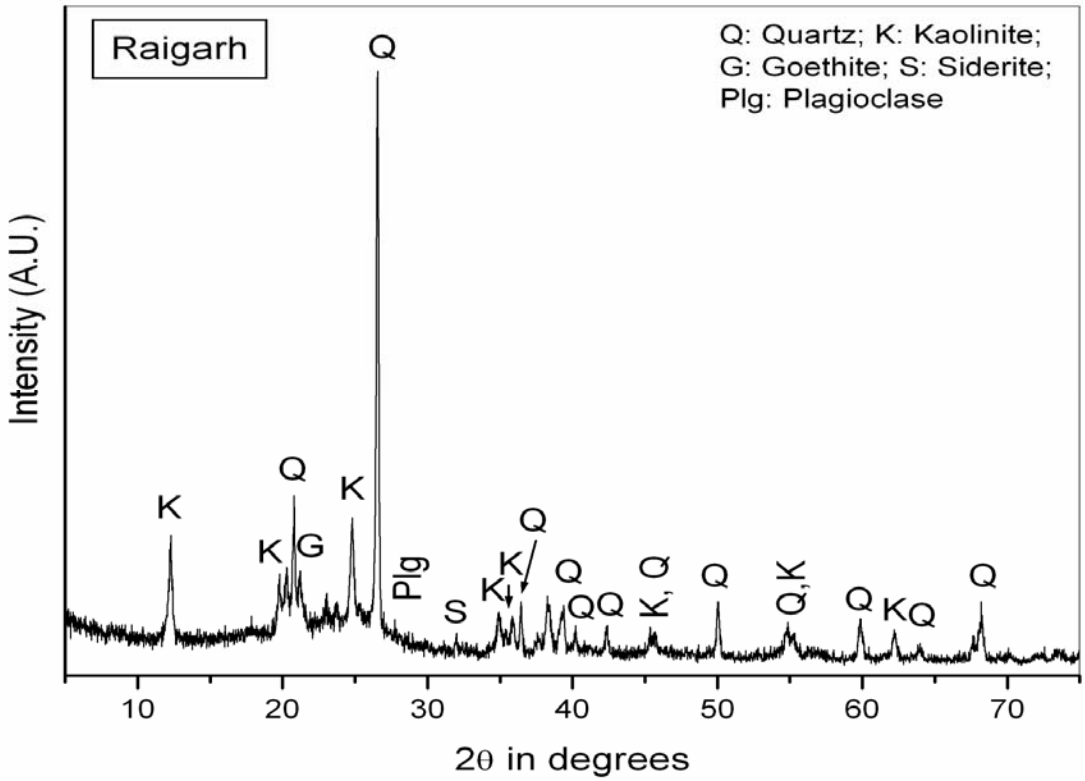

Fig.4.3 XRD pattern of Mand - Raigarh coalfield

The mineralogy of coal samples is tabulated in Table 4.1.

Table 4.1: Mineral phases in coal samples

Sl. No.	**Sample**	**Major Mineral Phases**	**Intermediate Mineral Phases**
1	Neyveli Lignite Coalfield	Kaolinite, Dolomite, Siderite	Bassanite, Haematite
2	Mand – Raigarh coalfield	Quartz, Kaolinite	Goethite, Siderite, Plagioclase
3	Rangit valley, Sikkim	Quartz, Muscovite, Illite	Plagioclase, Dolomite, Calcite, Siderite, Kaolinite

4.2 TRACE ELEMENT ANALYSIS:

4.2.1 MAND – RAIGARH COALFIELD:

The concentration of Cu in the sample was found to be well above the world average concentration. When compared to the Indian average, the Cu concentration is still higher in this sample. The crustal abundance of Cu is also lower than the concentration found in the sample. The total concentration of Zn was found to be well below the world average and crustal abundance. But, it is quite close to the average concentration of zinc in Indian coal. Ni concentration was found to be greater than the world average but well within the Indian average. The crustal abundance of Ni is much greater than that of the sample. The concentration of Cr is much higher than the world average, since in Indian coals Cr concentration is high. The crustal abundance is still higher. Pb concentration is well within the world average. When compared to crustal abundance and the Indian average, this coalfield has a higher concentration of Pb. The concentration of Mn is a little higher than the world average, though it is well within the Indian average (Table 4.2).

Table 4.2: Total element concentration of elements in coal samples (Unit: mg/kg)

Element	Mand-Raigarh	Rangit Valley	Neyveli Lignite	Crustal Abundance	World Average
Cu	**29.2**	8.6	10.4	25.0	15.0
Zn	36.9	30.2	21.4	65.0	50.0
Ni	**20.0**	**16.8**	**18.3**	56.0	15.0
Cr	**63.0**	**66.1**	**10.7**	126.0	10.0
Pb	17.5	9.7	8.2	14.8	25.0
Mn	**60.0**	**71.4**	18.5	716.0	50.0

4.2.2 RANGIT VALLEY, SIKKIM:

Concentration of Cu in Rangit valley is nearly half of the world average and Indian average concentration. It is much lower than the crustal abundance as well. The concentration of Zn is well below the world average and crustal abundance. Ni is present in higher concentration than the world average, though; the crustal abundance is much larger (Table 4.2). The concentration of Cr is much greater than the world average. Pb concentration is much lower than both the world average and crustal abundance. The concentration of Mn is also higher in Rangit valley when compared with the world average.

4.2.3 NEYVELI LIGNITE FIELDS:

Except for Ni and Cr, all other trace elements namely – Cu, Zn, Pb and Mn have much lower concentrations in lignite than their corresponding world average. While Cr is slightly higher in this lignite field, Ni is present is significantly higher concentrations (Table 4.2). All the trace elements are present in lower concentration than their crustal abundance.

4.3 MODE OF OCCURRENCE:

Results of the concentrations of each element under study after sequential extraction of coal samples of Rangit valley, Neyveli lignite and Mand-Raigarh coalfields is shown in Table 4.3.

Table 4.3: Concentration of elements in different extracts (Unit: in mg/kg)

Element	Sample	NH_4OAc	HCl	HF	HNO_3	Total
Cu	Mand-Raigarh	0	8.37	6.66	7.78	22.81
	Rangit Valley	0	1.34	2.70	2.44	6.48
	Neyveli Lignite	0	0.27	0.05	0.29	0.61
Zn	Mand-Raigarh	0.23	7.54	9.39	18.04	35.20
	Rangit Valley	0.12	10.50	6.50	8.41	25.23
	Neyveli Lignite	0.08	3.46	2.04	5.29	10.87
Ni	Mand-Raigarh	0.31	2.98	7.72	5.47	16.48
	Rangit Valley	0.07	5.09	4.80	5.07	15.03
	Neyveli Lignite	0.10	3.71	2.94	3.50	10.25
Cr	Mand-Raigarh	0	8.50	34.19	12.77	55.46
	Rangit Valley	0	14.31	30.77	15.06	60.14
	Neyveli Lignite	0	2.08	3.62	2.73	8.43
Pb	Mand-Raigarh	0.17	4.77	3.31	5.13	13.38
	Rangit Valley	0	3.84	0	1.75	5.59
	Neyveli Lignite	0	4.41	0	1.13	5.54
Mn	Mand-Raigarh	0.2	22.85	11.06	9.50	43.61
	Rangit Valley	0.8	34.35	12.50	8.75	56.40
	Neyveli Lignite	0.6	7.25	1.50	3.20	12.55

4.3.1 COPPER:

In both Rangit valley and Mand- Raigarh samples, Cu was pre-dominantly leached by HCl and HNO_3 (Figure 4.4). This indicates the primary mode of occurrence of Cu as disulphides and sulphides which conform to the mode of occurrence suggested by Swaine and Goodarzi (1995). But in Neyveli lignite, Cu was leached in neither of the acids which suggest that it

may be either shielded by the organic matrix, or may be present as insoluble minerals or as organo-metallic complexes (Table 4.3).

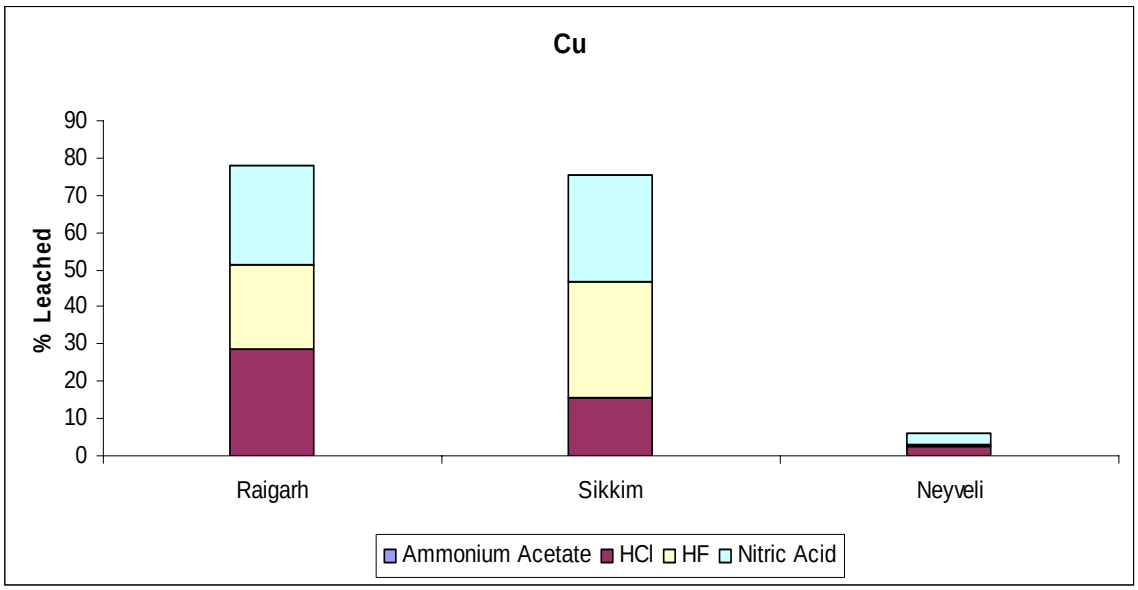

Fig 4.4: Distribution of Cu in coal

4.3.2 ZINC:

Major mode of occurrence of Zn is in the form of disulphides, sulphides and silicates in both Rangit valley and Mand- Raigarh coalfield (Figure 4.5). Since a large percentage of Zn was not leached, it is inferred that it may be present as insoluble minerals and/or shielded by organic matrix.

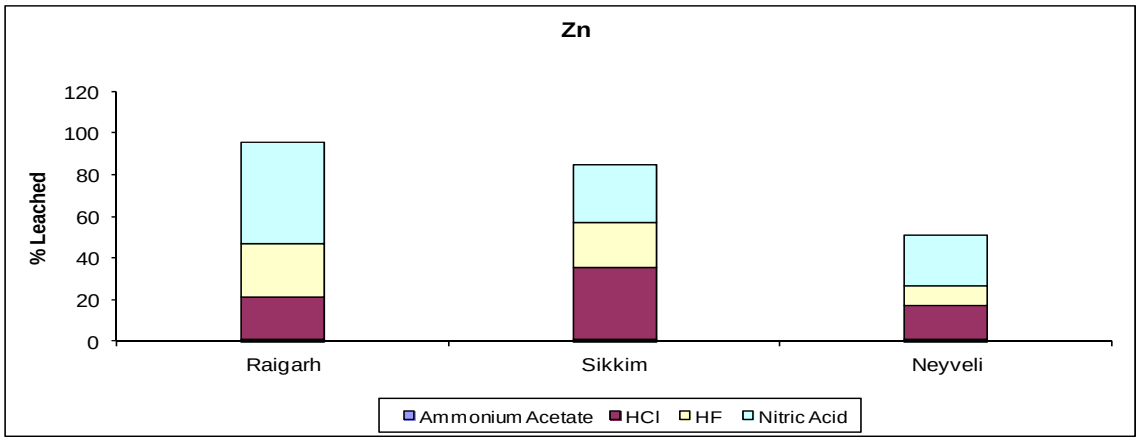

Fig 4.5: Distribution of Zn in coal

4.3.3 MANGANESE:

As cited by Swaine and Goodarzi (1995), the primary mode of occurrence of Mn is in the form of carbonates (Figure 4.6). It is observed that a substantial amount of Mn was not leached from all the coal samples which indicate towards organic association. But in lignite sample, the percentage of Mn in ammonium acetate filtrate was noticeable which indicates an adsorbed and/or exchangeable phase.

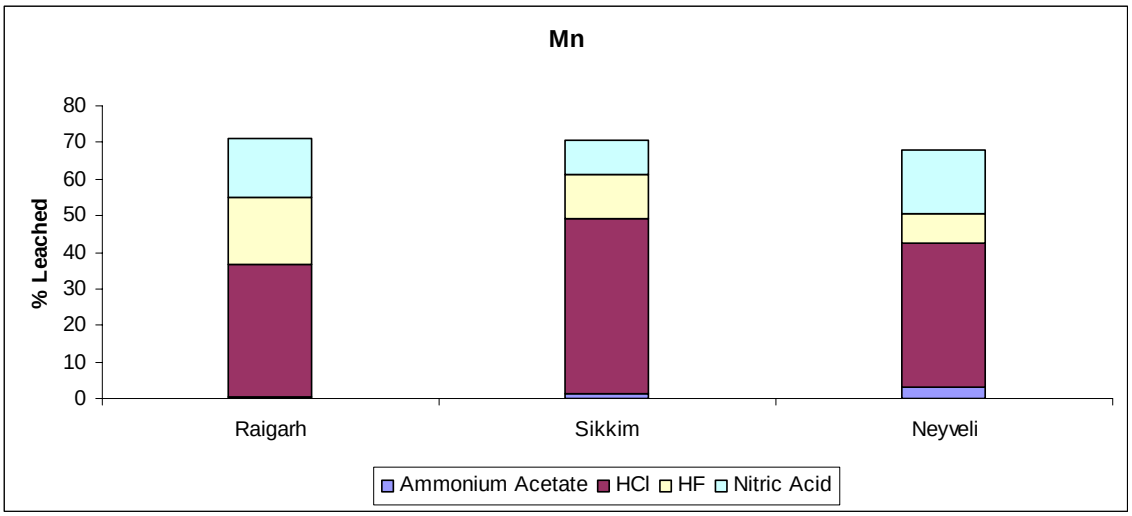

Fig 4.6: Distribution of Mn in coal

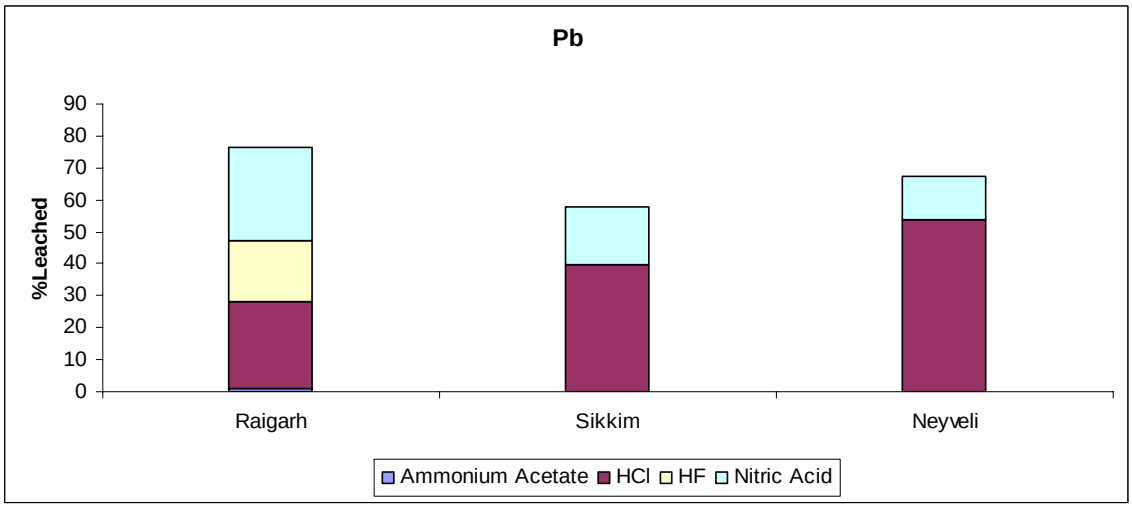

Fig 4.7: Distribution of Pb in coal

4.3.4 LEAD:

Primary mode of occurrence of Pb was found to be sulphides and disulphides (Figure 4.7). Fair amount of Pb was not leached from the samples of Ranjit valley coal fields and Neyveli Lignite fields. This indicates that Pb may be shielded by organic matrix or be present as insoluble minerals or may be present in the form of organo-metallic complex.

4.3.5 NICKEL:

Primary mode of occurrence of Ni was found to be sulphide and silicates in case of both Rangit valley and Mand- Raigarh coalfields (Figure 4.8). But in Neyveli lignite sample, major amount of Ni was not leached and thus, it can be concluded that it may be organically associated in this sample.

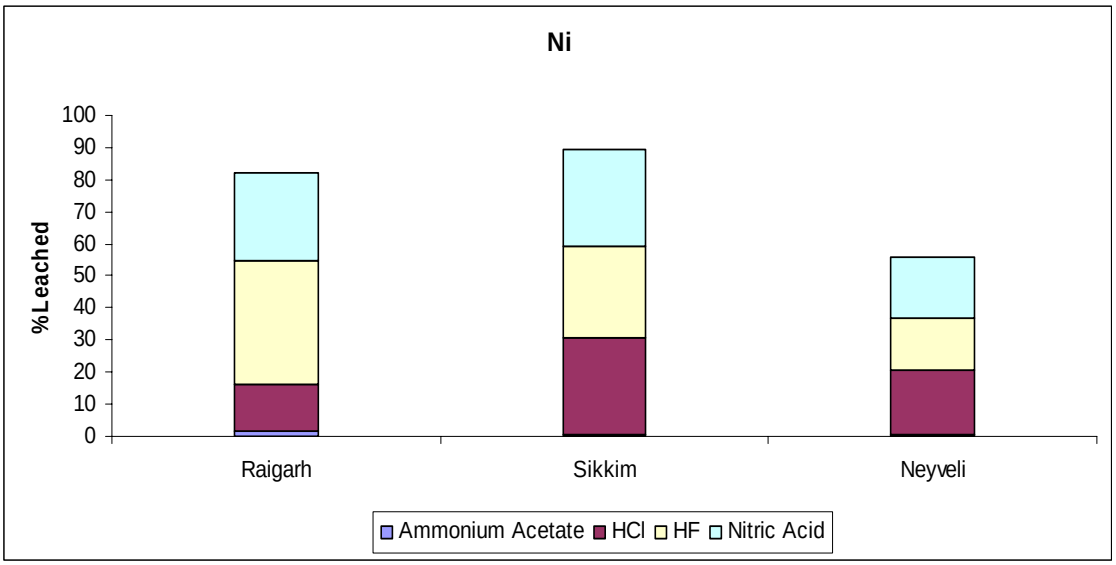

Fig 4.8: Distribution of Ni in coal

4.3.6 CHROMIUM:

Major amounts of Cr were leached by HF followed by HNO_3 in all the samples (Figure 4.9). Thus it is inferred that Cr is associated with silicates. Substantial amount of Cr is also present in form of disulphides. In the Neyveli lignite sample, about one – fifth of Cr was not leached which indicates towards presence of organically associated Cr.

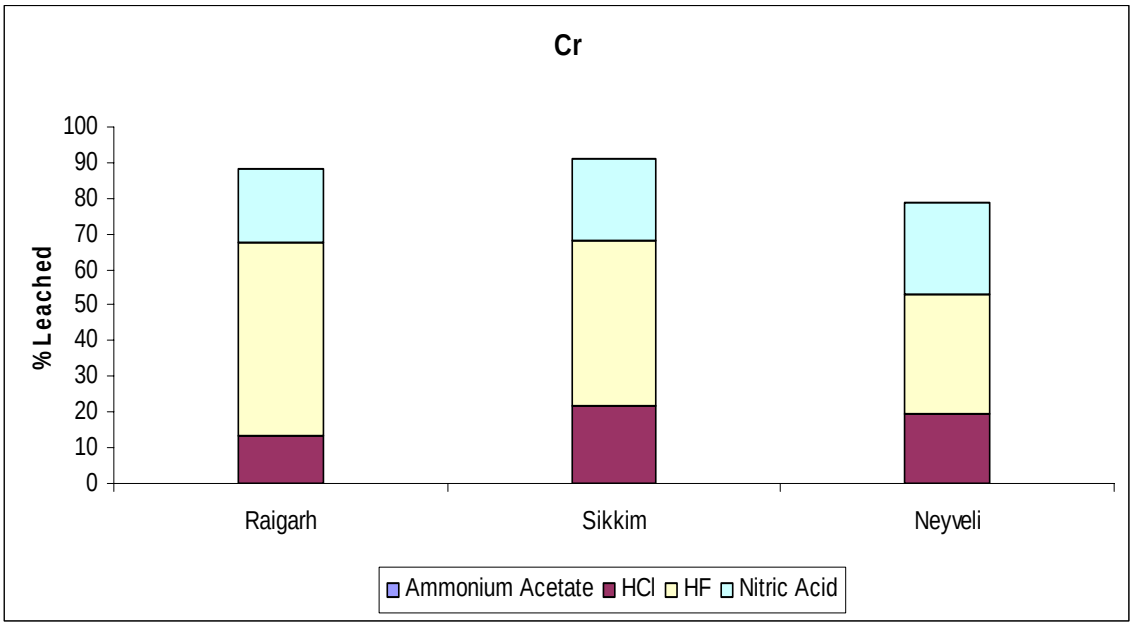

Fig 4.9: Distribution of Cr in coal

Table 4.4: Mode of occurrence of elements in coal samples

Element	Mand-Raigarh	Rangit Valley	Neyveli Lignite
Cu	Sulphides, disulphides, clay minerals, organic association	Sulphides, disulphides, clay minerals, organic association	Shielded by organic matrix, organo-metallic complex
Zn	Sulphides, disulphides, silicates	Sulphides, disulphides, silicates	Sulphides, insoluble minerals, organo-metallic complex
Mn	Carbonates, organic association	Carbonates, organic association	Carbonates, organic association, adsorbed or exchangeable
Pb	Sulphides, disulphides	Sulphides, disulphides, Shielded by organic matrix, insoluble minerals, organo-metallic complex	Sulphides, Shielded by organic matrix, insoluble minerals, organo-metallic complex
Ni	Silicates, sulphides	Silicates, sulphides	Organic association, sulphides
Cr	Silicates, clay association, disulphides	Silicates, clay association, disulphides	Organic association, silicates, clay association, disulphides

Chapter-5:

CONCLUSIONS

5 CONCLUSIONS:

Quartz and clay minerals (kaolinite, illite, and muscovite) were found to be the major mineral phases in all coal samples. Concentration of Ni and Cr were higher than the world average in all three coal samples. Cu concentration in Raigarh and Mn concentration in both Raigarh and Rangit valley were greater than the world average. Primary mode of occurrence of Cu, Zn and Pb was found to be sulphides and disulphides in Raigarh and Rangit valley samples. Primary mode of occurrence of Cr and Ni were organic association in lignite sample. In the other two samples they were associated with clay and silicates. Mn occurred mainly in the form of carbonates.

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